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THERMAL STABILITY STUDIES ON HIGH EXPLOSIVES BY ACCELERATING RATE CALORIMETRY

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Canadian Explosives Research Laboratory

December 1983

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48 pp

ADMINISTRATION OF THE CANADA EXPLOSIVES ACT
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THERMAL STABILITY STUDIES ON HIGH EXPLOSIVES BY
ACCELERATING RATE CALORIMETRY

by

P.P. Lee* and R.R. Vandebeek**

ABSTRACT

The thermal stability of six high explosives: PETN, RDX, Tetryl, TNT, Nitroguanidine and Guanidine nitrate were studied using an accelerating rate calorimeter (ARC). The tendency of decomposition under selected heating logics, experimental systems and thermal inertia was examined. Comparing the decomposition data obtained using the ARC to literature values cited for other techniques, the thermal decompositions detected by the ARC occurred at lower temperatures. Infrared spectra of original compounds and the residues from thermal decomposition were compared.

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ETUDES SUR LA STABILITÉ THERMIQUE D'EXPLOSIFS SECONDAIRES AU MOYEN
DE LA CALORIMÉTRIE À RÉGIME ACCÉLÉRÉ

par

P.P. Lee* et R.R. Vandebeek**

RÉSUMÉ

Pour l'étude de la stabilité thermique de six sortes d'explosifs secondaires tels le PETN, le RDX, le tétryl, le TNT, la nitroguanidine et le nitrate de guanidine on fit usage du calorimètre à régime accéléré (CPA). On observa la tendance à la décomposition de ces substances à l'aide de méthodes spécifiques d'échauffement de l'échantillon, de systèmes empiriques et de l'inertie thermique. En comparant les valeurs publiées sur la décomposition résultant de d'autres techniques avec les données obtenus avec le CRA on nota que les décompositions thermiques décelées par ce dernier, avaient lieu à des températures moins élevées.

Le spectre infrarouge de composés originaux ainsi que les résidues de la décomposition thermique furent aussi comparés.

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INTRODUCTION

An understanding of the potential thermal hazards of high explosives is imperative for their safe manufacturing, handling and usage. Thermal decomposition of high explosives has been studied extensively using a number of different techniques. The traditional techniques for studying thermal stability of energetic materials include differential scanning calorimetry (DSC), differential thermal analysis (DTA), thermal gravimetry (TG), gas evolution (GE) and electron paramagnetic resonance (EPR). They have relative strengths and shortcomings. For example, the composition of a sample of a few milligrams taken from a grossly heterogeneous suspension is not necessarily representative of the whole mass in microanalytical techniques. There are other limitations to the DSC technique that the data are obtained at a fixed heating rate which forces the reaction to occur at higher temperatures. In addition, pressure data are not commonly available by DSC technique.

Since no single test method can establish the sensitivity of an explosive to thermal effect, accelerating rate calorimetry is another approach in the evaluation of thermal runaway reactions. It is an automated laboratory instrument which aides in experimentally determining the time, temperature and pressure relationships of any exothermic reaction in an adiabatic environment. ARC has the advantage of pressure monitoring, and a larger sample of heterogeneous compositions can be used. This study reports on the use of accelerating rate calorimetry to evaluate the thermal hazards of several high explosives.

Different approaches have been utilized in the past to obtain information on exothermic reactions. The literature values for the thermal decomposition of several high explosives using various techniques are compared in Table 1.

Table 1 - Comparison of literature values on thermal decomposition of high explosives by different techniques

Sample/technique	Decomposition temperature (°C)	E(Kcal/mole)	Reference
<u>PETN</u>			
ARC	112 ($\phi = 1$, initial temp.)	54.5	5
DSC	180 (onset temp.)	-	8
DSC	200-203 (critical temp.)	47.0	9
DTA	160 (autoignition)	33.0	12
-	161-233 (isothermal decomp.)	47.0	10
-	137-157 (isothermal decomp.)	38.6	10
<u>RDX</u>			
ARC	180 ($\phi = 1$, initial temp.)	173.0	5
DSC	214 (onset temp.)	-	8
DSC	215-217 (critical temp.)	47.1	9
DSC	210-261	45.2	17
DSC	207-252	53.0	18
DTA	197 (autoignition)	34.0	12
EPR	175-205 (intermediate radical generation)	-	11
GE	170-198	49.0	11
GE	207-227	55.6	11
-	213-299 (isothermal decomp.)	47.5	10
<u>Tetryl</u>			
DSC	185 and 263 (onset temp.)	-	8
DSC	170-174	58.0	17
-	211-260 (isothermal decomp.)	38.4	10
-	132-164 (isothermal decomp.)	34.9	10

Table 1 (cont'd)

Sample/technique	Decomposition temperature (°C)	E(Kcal/mole)	Reference
<u>TNT</u>			
DSC	309 (onset temp.)	-	8
DSC	287-289 (critical temp.)	34.4	9
DSC	245-269 (isothermal)	29.4	16
DTA	275 (autoignition)	24.0	12
DTA	270	-	14
DTA	270	-	15
TG	250	-	15
-	275-312 (isothermal decomp.)	34.4	10
-	237-277 (isothermal decomp.)	43.4	10
<u>Nitroguanidine</u>			
DSC	200-204	20.9	9
Explosion temp.	275 (decomposition)	-	19
<u>Guanidine nitrate</u>			
DTA	305	-	13
TG	275-325	-	13

EXPERIMENTAL

The accelerating rate calorimeter was developed by the Dow Chemical Company and licensed to Columbia Scientific Industries of Austin, Texas. Since the design, operation and performance have been published elsewhere [1-5], only a brief discussion of the instrumental design and the operational logic follow.

The operation of the ARC involves a sample in a bomb where the bomb plus contents is maintained adiabatically with respect to its environment. In order to achieve an adiabatic condition over a temperature range of ambient to 500°C and temperature rates of 0.02°C/min to 10°C/min, the ARC uses a digitally controlled thermocouple/heater feedback system. Figure 1(a) illustrates

the original calorimeter assembly and sample system. The jacket is composed of three zones, top, side and bottom which are individually heated and controlled by Nisil/Microsil (type N) thermocouples. The thermocouples are cemented on the inside surface of the jacket and the same type of thermocouple is clamped directly on the outside surface of the bomb. All the thermocouples are referenced to the ice point which is designed to be stable to within 0.01°C . The placement of the bomb thermocouple has to be repeatable in every experiment. In normal operation, without extreme care, the thermal contact is not very reproducible. This causes highly undesirable random scattering of the calibration curves and drifting problems during the run. The drift corrections are performed normally every 50°C for the entire temperature range by applying the required offset voltage. The pressure of the reaction system is monitored with a 0-2500 psi pressure transducer. For safety precautions, the entire calorimeter is mounted inside a containment vessel.

As difficulties were encountered with pressure measurement while studying molten materials, the calorimeter was modified to overcome this problem. An illustration of the modification is presented in Fig. 1 (b) and it was used in this thermal stability study of high explosives. The pressure measurement system was modified to provide a low dead volume, totally disposable connection between the sample container and the pressure transducer. A piece of 1/16 in. (0.159 cm) O.D. tubing was fitted through the original fixed bomb adaptor. One end was hooked up to the pressure transducer which was modified to reduce the dead volume. The other end was silver soldered to a cap for connecting the 3/16 in. (0.476 cm) neck of the bomb. The 1/16 in. (0.159 cm) tubing and the cap could be easily replaced whenever it was necessary. This modification could reduce the hazard of damaging the original fixed bomb adaptor and the blockage problem of the pressure measurement system. The 1/8 in. (0.317 cm) O.D. neck of the 1 in. (2.54 cm) diameter Hastelloy C spherical bomb (~19 g) was converted to 3/16 in. (0.476 cm) to minimize difficulties in loading solid materials.

Several types of sample containers can be used in the ARC depending on the material being tested. The light weight titanium bomb (~8 g) is used when low thermal inertia is desired and the Hastelloy C cylindrical bomb (~50 g) can be used for viscous or solid samples.

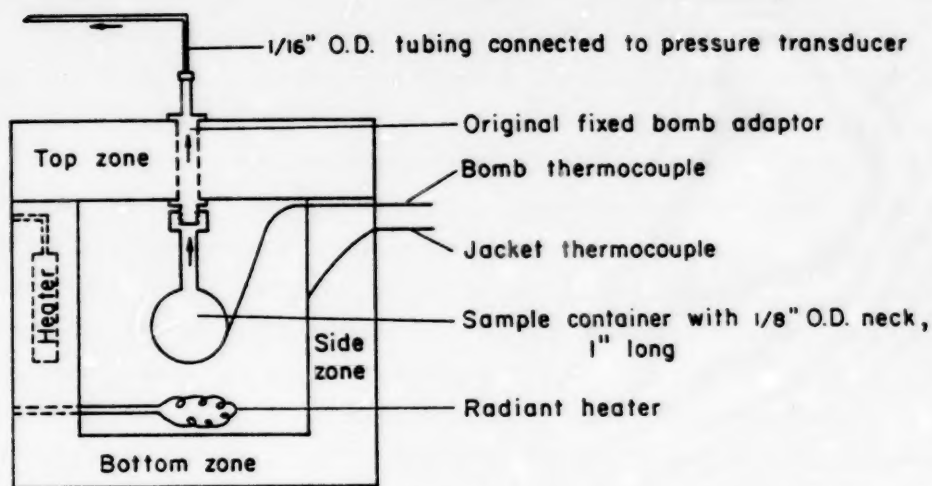


Fig. 1(a) - Original calorimeter assembly and sample system.

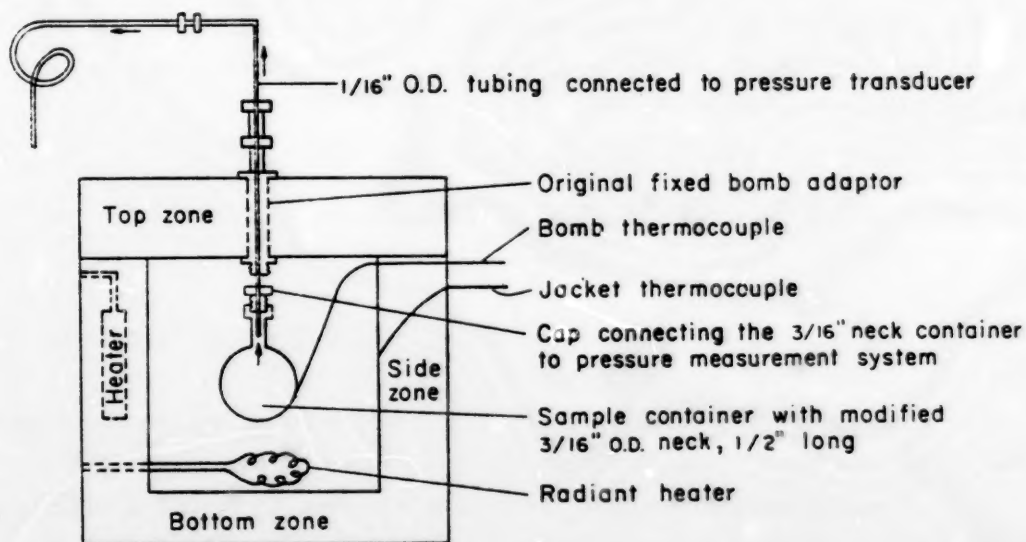


Fig. 1(b) - Modified calorimeter assembly and sample system.

The heat-wait-search operational logic of the ARC is shown in Fig. 2. The ARC is first heated to a desired starting temperature and held a period of time for thermal equilibrium to be achieved before a rate search is performed. If the rate is less than the user-selected threshold, usually 0.02°C/min, the ARC will proceed automatically to the preselected temperature step heat-wait-search sequence. When a self-heat rate greater than the preset rate is detected, the calorimeter will be maintained at adiabatic conditions until the completion of the reaction. After detection of an exotherm, time, temperature, and pressure data are collected automatically. At the conclusion of each run, the relevant data could be plotted by the ARC microprocessor.

Isothermal age method is also available. The system is maintained adiabatically at a pre-determined temperature for a period of time. The system goes into the data acquisition mode if a self-heat rate greater than 0.02°C/min is detected during the aging. The isothermal age study measures the maximum temperature at which a material is stable for certain periods of time and the effect of accumulated products on decomposition.

In experiments with the ARC, part of the heat generated by the exothermic reaction is used in raising the temperature of the bomb and this aspect must be taken into account. The thermal inertia, ϕ , is a critical factor in the analysis where data must be corrected to allow for the effect of the test bomb heat capacity on the response of the system. In an ideal case, ϕ is equal to 1.

$$\phi = 1 + \frac{C_{v(\text{bomb})} M_{(\text{bomb})}}{C_{v(\text{sample})} M_{(\text{sample})}}$$

Figure 3 demonstrates the thermal inertia effect on the time to maximum rate curve.

Due to the explosive properties, ϕ could only be chosen as close to real situations that would result in minimal damage to the calorimeter.

The high explosives used for this study were technical grade without further purification and they were stored at room temperature before the test. The samples consisted of the following:

1. Pentaerythritol tetranitrate (PETN), super fine.
2. Cyclotrimethylene trinitramine (RDX), British.

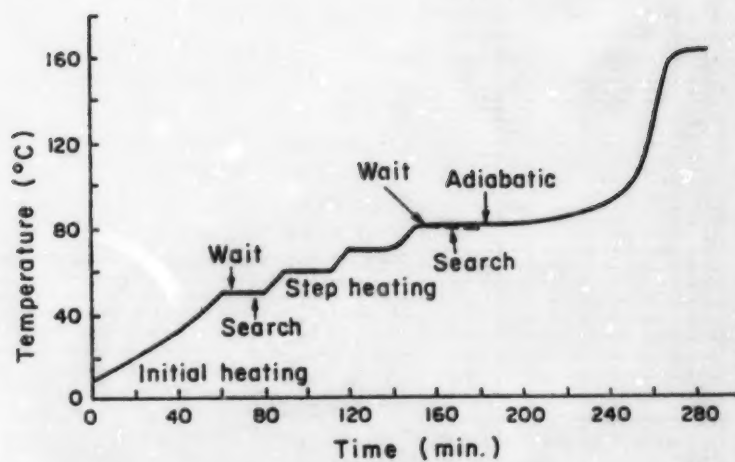


Fig. 2 - The heat-wait-search operation mode of an accelerating rate calorimeter.

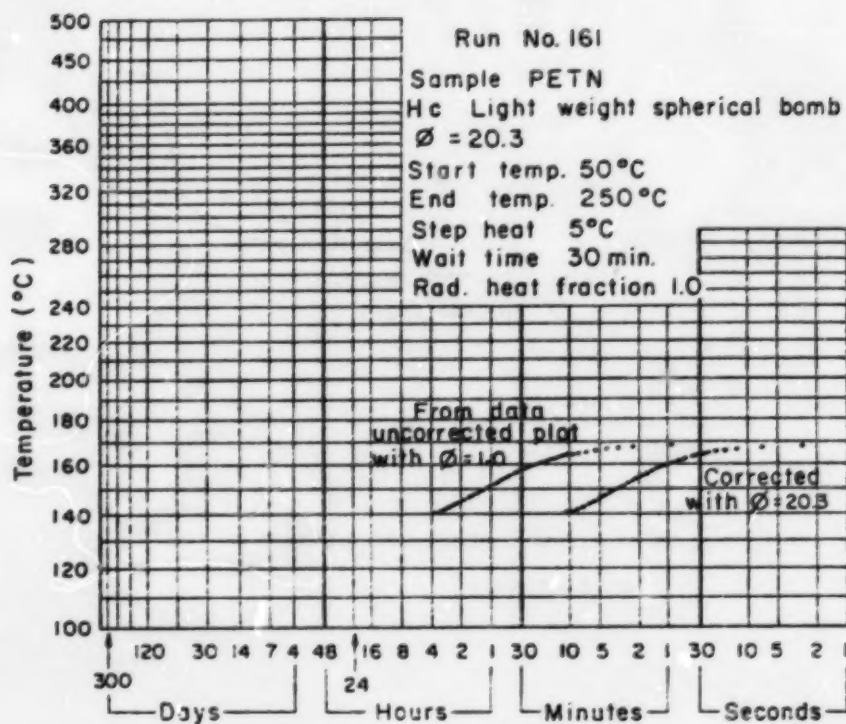


Fig. 3 - Time to maximum rate plot.

3. 2, 4, 6 - Trinitrophenylmethylnitramine (Tetryl).
4. Trinitrotoluene (TNT), CERL reference.
5. Nitroguanidine.
6. Guanidine nitrate.

All experiments for high explosives were conducted in the modified light weight Hastelloy C spherical bomb under air atmosphere. As shown in Fig. 1(b), the sample and container was tightly connected to a pressure measuring line. It was termed "confined" system so that the pressure change due to the decomposition and the effect of accumulated products could be monitored. Some tests were performed in a "non-confined" system at which the sample bomb was loosely hooked to the pressure measurement line. In this case, the sample was not subjected to pressure greater than atmospheric pressure.

PREVIOUS WORK

A study on thermal stability of nitrocellulose (NC) by an ARC was reported [6]. A titanium 0.032" (0.081 cm) wall spherical bomb, weighing approximately 7 g with an opening at the top and self-adhesive Teflon tape sealing, was used in the study. The runs started at 130°C and ended at 180°C with a heat step of 2°C. Sensitivity was 0.02°C/min. The lowest initial temperature of an exotherm was detected at 136.5°C with ϕ equal to 6.4. No ignition occurred as ϕ increased to 80.4. Figure 4 demonstrates the effect of thermal inertia on the initial temperature of NC decomposition.

An ARC had been used to examine the thermal stability of different types of ammonium nitrate (AN) and ammonium nitrate-fuel oil (ANFO) explosives [7]. In order to minimize the sample loading difficulties and the blockage problems with the pressure measuring connection, a Hastelloy C cylindrical bomb was used. However, there was a disadvantage with this system as no pressure could be determined. Step heat was employed for the study. After equilibrium at 100°C, an iterative "5°C heat - 20 min wait-search" sequence was conducted until the heat rate was greater than 0.02°C/min. The major exothermic decomposition occurred above 210°C as the results are summarized in Table 2.

Parameters :

Open Ti bomb with Teflon tape closure
Sensitivity 0.02 °C/min
Step heat 2 °C
Start temperature 130 °C
End temperature 180 °C
Rad. heat fraction 0.5
Wait time 10 minutes

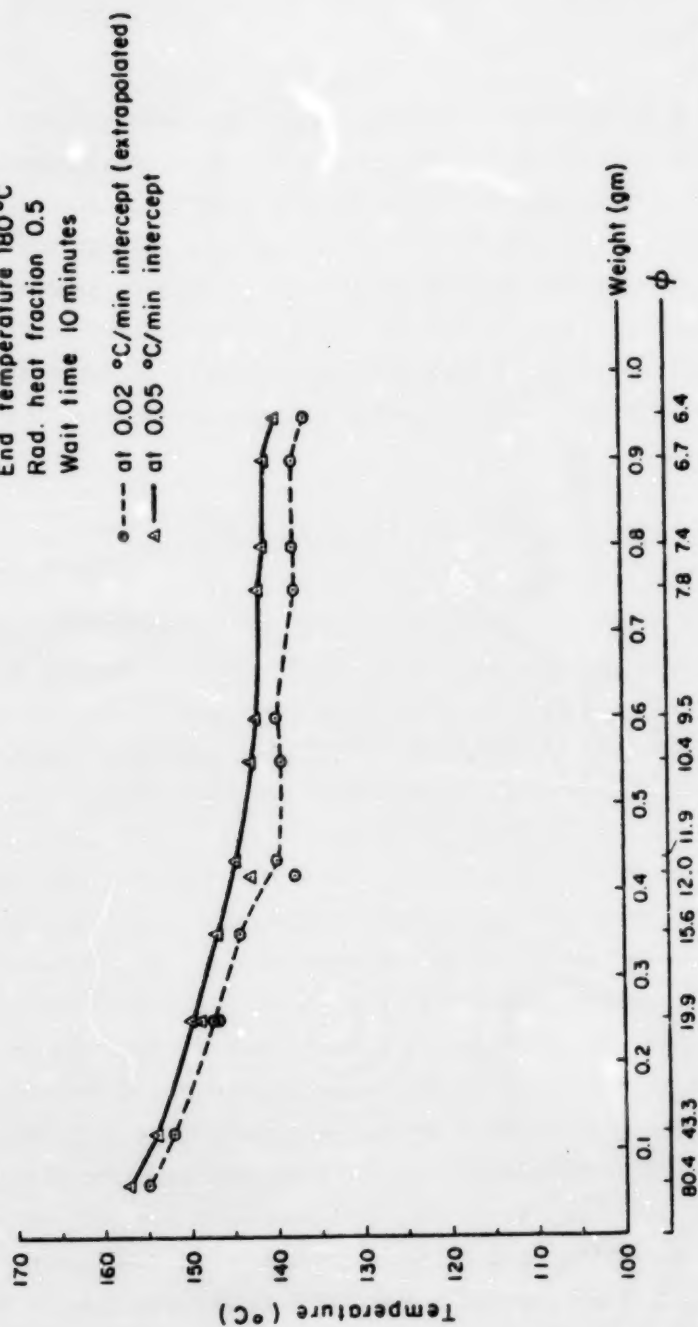


Fig. 4 - Effect of thermal inertia (ϕ) on the initial temperature of NC decomposition.

Table 2 - ARC results on AN and ANFO decomposition by step heat logic

Run no.	ϕ	1st exotherm but stop (°C)	Initial data			Before ignition			$\Delta T_{AB,S}$ (°C)
			T_o (°C)	m_o (°C/min)	t_o (min)	T (°C)	m (°C/min)	$t_o \rightarrow t$ (min)	
<u>AN granular</u>									
86*	7.0	191.03	204.10	0.030	920.84	230.28	2.032	368.82	72.56
85*	9.0	190.90	197.42	0.023	829.64	231.63	2.000	525.47	78.60
99	9.0	196.01	218.82	0.033	1161.76	260.89	2.157	368.43	72.29
<u>AN aeroprills</u>									
92	9.2	206.04	214.23	0.044	941.72	251.37	2.068	218.73	67.77
95	9.0	201.07	215.59	0.028	1013.43	259.63	2.000	585.63	78.39
124	9.2	206.03	212.39	0.025	962.51	255.91	2.000	635.74	77.72
<u>AN-C prills, C.I.L.</u>									
130	9.2	201.14	225.20	0.039	1282.12	262.74	1.904	251.82	68.11
134	9.0	196.21	218.61	0.031	1136.74	262.70	2.000	355.85	77.39
<u>ANFO, Nitrite FR, DuPont</u>									
128	9.2	191.09	234.54	0.028	1317.62	244.35	0.561	161.27	20.51
129	9.0	201.13	238.34	0.044	1248.60	252.42	1.952	166.36	28.93
<u>ANFO, AMEX II, C.I.L.</u>									
131	9.0	196.10	228.18 (ignited during step heat)			235.00	0.344	61.35	-
133	9.2	186.09	229.05	0.071	1668.56				-

* Run no. 85 and 86 were sealed with Teflon disk only.

RESULTS AND DISCUSSION

STEP HEAT STUDIES

The thermal stability of six high explosives was studied by step heat logic. After equilibrium at the start temperature, an iterative "5°C heat - 30 min wait-search" sequence was conducted until the appearance of a heat rate greater than 0.02°C/min. After detection of an exotherm, time, temperature and pressure were monitored continuously until the end of the reaction. The sample size used ranged from 0.25 g to 0.50 g depending on the reactivity of the material. Initial temperature, self-heat rate, pressure change, effect of thermal inertia and experimental systems were studied. The materials were tested under "confined" and "non-confined" systems as described earlier. Table 3 summarizes the thermal decomposition data of high explosives obtained using step heat method.

Table 3 - Thermal decomposition data of high explosives by step heat method

Run no.	ϕ^a	Run parameters		Initial data			Before ignition			At maximum rate			$\Delta T_{AB,S}$ (°C)	Wt loss %			
		system	start heat temp. step (°C)	T_o (°C)	m_o (°C/min)	t_o (min)	T (°C)	$\dot{m}$ (°C/min)	P (psia)	P (MPa)	T_m (°C)	$\dot{m}_m$ (°C/min)			P _m (psia)	P _m (MPa)	
PETN																	
158	20.4	confined	50	5	147.10	0.072	941.09	175.12	2.105	29.7	0.20	180.72	75.823	117.7	0.81	37.54	72.0
149	11.4	"	50	5	148.44	0.154	907.86	176.07	9.166	25.2	0.17	195.24	293.500	495.7	3.42	54.19	86.7
145	19.4	non-confined	50	5	141.34	0.036	855.49	no ignition				173.88	0.893	-	-	42.21	91.7
161	20.3	"	50	5	140.89	0.023	908.63	no ignition				168.90	0.408	-	-	34.63	91.3
RDX																	
147	19.0	confined	100	5	Ignited at 200°C "wait" cycle											-	100
154	18.0	"	190	2	197.49	0.056	158.34	201.63	5.625	41.6	0.29	244.13	663.666	1016.0	7.00	80.68	91.8
163	18.7	non-confined	190	2	Ignited at 198°C "wait" cycle							Explosion				-	-
TETRYL																	
150	19.3	confined	50	5	146.61	0.045	902.38	no ignition				161.13	0.233	89.5	0.62	22.74	-
					210.58	0.032	1531.86	no ignition				225.60	0.117	264.7	1.83	21.82	-
152	11.4	"	50	5	141.02	0.023	894.52	no ignition				169.12	1.312	83.3	0.57	-	-
					continuous curve			no ignition				237.53	0.312	79.2	0.55	122.26	76.9
156	11.8	"	50	5	141.54	0.042	878.98	no ignition				175.13	2.500	138.9	0.96	56.85	-
					218.86	0.190	1372.97	no ignition				249.37	1.576	261.6	1.80	55.07	73.2
155	7.4	"	50	5	136.19	0.030	844.92	no ignition		168.1	1.16	Explosion				47.12	-
164	13.0	non-confined	50	5	141.44	0.035	873.69	no ignition				168.49	0.784	-	-	-	-
					continuous curve			no ignition				234.46	0.155	-	-	115.07	76.2
TWT																	
159	20.4	confined	50	5	226.12	0.039	1677.82	254.15	3.500	146.8	1.01	268.82	223.500	534.1	3.68	54.70	74.5
153	10.0	"	50	5	207.58	0.031	1701.86	258.10	13.000	179.1	1.23	280.01	355.166	1546.2	10.66	106.54	-
162	19.9	non-confined	50	5	225.91	0.022	1671.95	no ignition				249.58	1.500	-	-	32.48	67.0

Table 3 - (cont'd)

Run no.	ϕ^a	Run parameters		Initial data			Before ignition			At maximum rate			$\Delta T_{AB,S}$ (°C)	Wt loss %			
		system	start temp. (°C)	heat step (°C)	T_o (°C)	$\dot{m}_o$ (°C/min)	t_o (min)	T (°C)	$\dot{m}$ (°C/min)	P (psia)	P (MPa)	T_m (°C)			$\dot{m}_m$ (°C/min)	P _m (psia)	P _m (MPa)
Nitroguanidine																	
165	20.9	confined	50	5	165.93	0.043	1094.24	170.58	4.083	85.2	0.59	172.39	28.500	175.6	1.21	14.86	66.0
166	17.7	"	50	5	161.05	0.020	1068.17	168.55	9.333	200.4	1.38	170.11	21.000	242.7	1.67	17.27	65.6
171	17.8	"	50	5	166.28	0.058	1109.17	170.43	3.187	266.7	1.84	171.63	33.000	289.4	1.99	15.38	65.3
169	19.1	non-confined	50	5	198.71	0.042	1481.95	no ignition				201.71	0.063	-	-	3.75	65.4
170	18.5	"	50	5	202.04	0.069	1424.45	no ignition				204.64	0.117	-	-	3.20	65.0
Guanidine nitrate																	
174	17.6	confined	50	5	251.71	0.055	1881.04	no ignition				271.32	0.476	blockage	-	26.68	85.3
176	11.4	"	50	5	251.54	0.051	1902.74	no ignition				299.60	2.050	167.2	1.15	48.27	100

^a $C_{v,bomb} = 0.1 \text{ cal } ^\circ\text{C}^{-1} \text{ g}^{-1}$ for Hastelloy C and $C_{v,sample} = 0.5 \text{ cal } ^\circ\text{C}^{-1} \text{ g}^{-1}$.

PETN was tested and the initial decomposition was detected at about 141°C by non-confined system and 147°C by confined system depending on the initial rate detected. Figure 5 is an example of PETN decomposition curves. It indicated that the self-heat rate and pressure of the sample/container system started to increase slowly at 147°C. The sample ignited rapidly about 175°C and produced fast self-heat rate and pressure build-up. Effect of thermal inertia and experimental system for PETN decomposition are demonstrated in Fig. 6. The decomposition reaction slowed down in the non-confined system tests but the sample ignited in the tests using the confined system. This phenomenon suggested that the decomposition was accelerated by the accumulated decomposition products and pressure. Although the thermal decomposition kinetics of PETN have been studied repeatedly, there is no general agreement about the decomposition mechanism or on the values of its Arrhenius parameters.

RDX was first heated to 190°C, then step heated 2°C and searched for exotherm after equilibrium. It was stable below 195°C but the self-heat rate increased above 195°C even though it was below the threshold sensitivity 0.02°C/min. The decomposition was so abrupt that during some tests the samples ignited during the "wait" step. An exotherm of RDX decomposition was detected at about 197°C with pressure build-up over 1000 psia at ignition. The data of self-heat rate, pressure and pressure rate versus temperature are plotted in Fig. 7. It shows the reaction was very fast and the ignition took place only shortly after the initial onset temperature. For the experiment with the non-confined system, the more vigorous ignition shifted the lid of the calorimeter. The thermal decomposition of RDX was detected below its melting point at 195°C which agreed with other investigators [20,21].

McGuire and Tarver deduced the chemical decomposition model for the thermal explosion of confined RDX [22]. The available data suggests the decomposition takes place in three steps. The first step is the endothermic breaking of C-N bonds in the ring forming $H_2C = N - NO_2$. The second major step is the slightly exothermic rearrangement $H_2C = N - NO_2$ into either CH_2O and N_2O or HCN and HNO_2 . The third major step is the very exothermic gas phase decomposition into the stable gaseous products H_2O , N_2 , CO , CO_2 etc. The thermal decomposition studied by ARC detected the exothermic reaction. Thus the RDX decomposition model is:



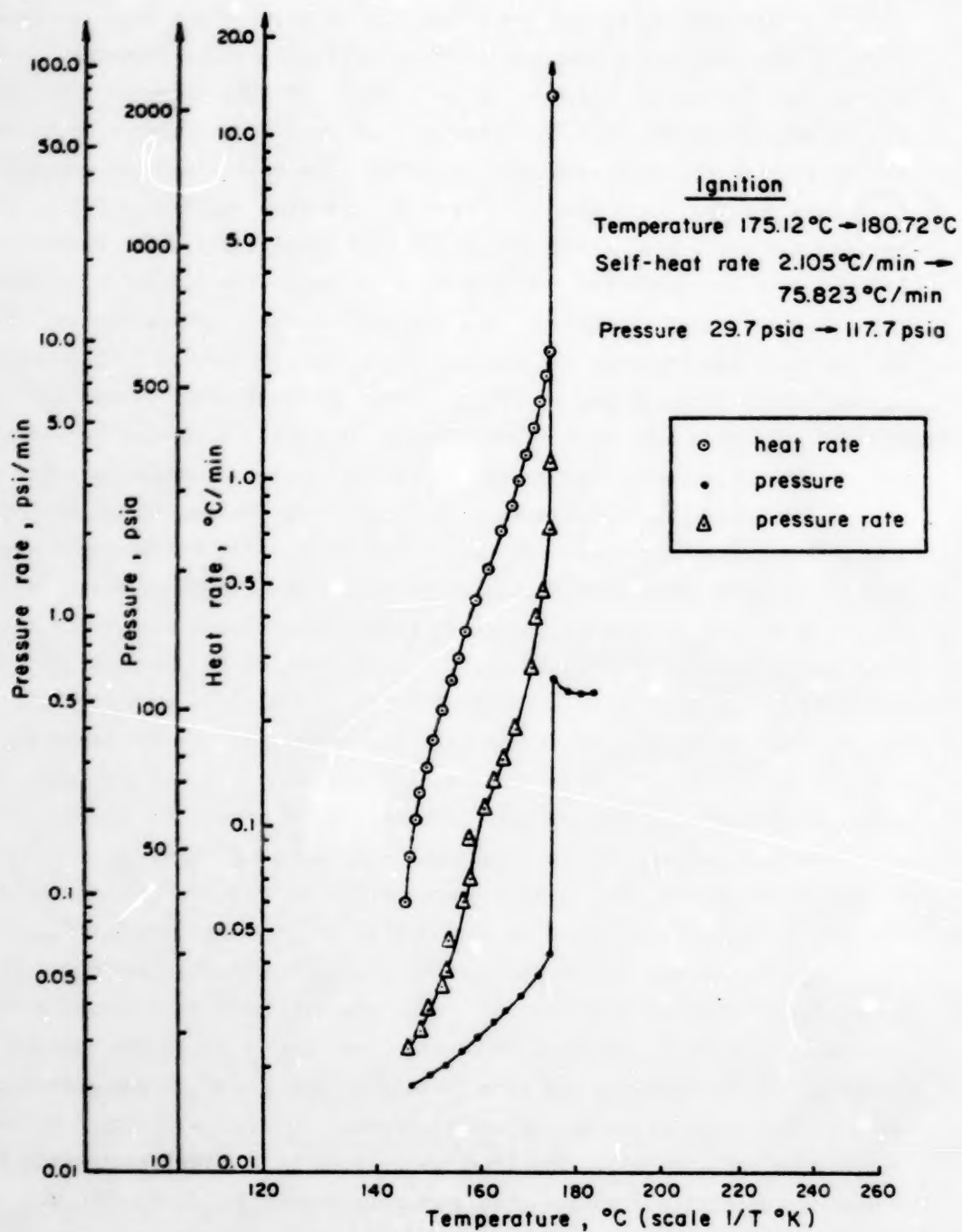


Fig. 5 - PETN, data plots from ARC experiment run no. 158, confined system, sample 0.2401 g, $\phi = 20.4$, 19.4190 g Hastelloy C spherical bomb, air atmosphere, 50°C start temperature, 5°C step heat interval, 30 minutes wait time.

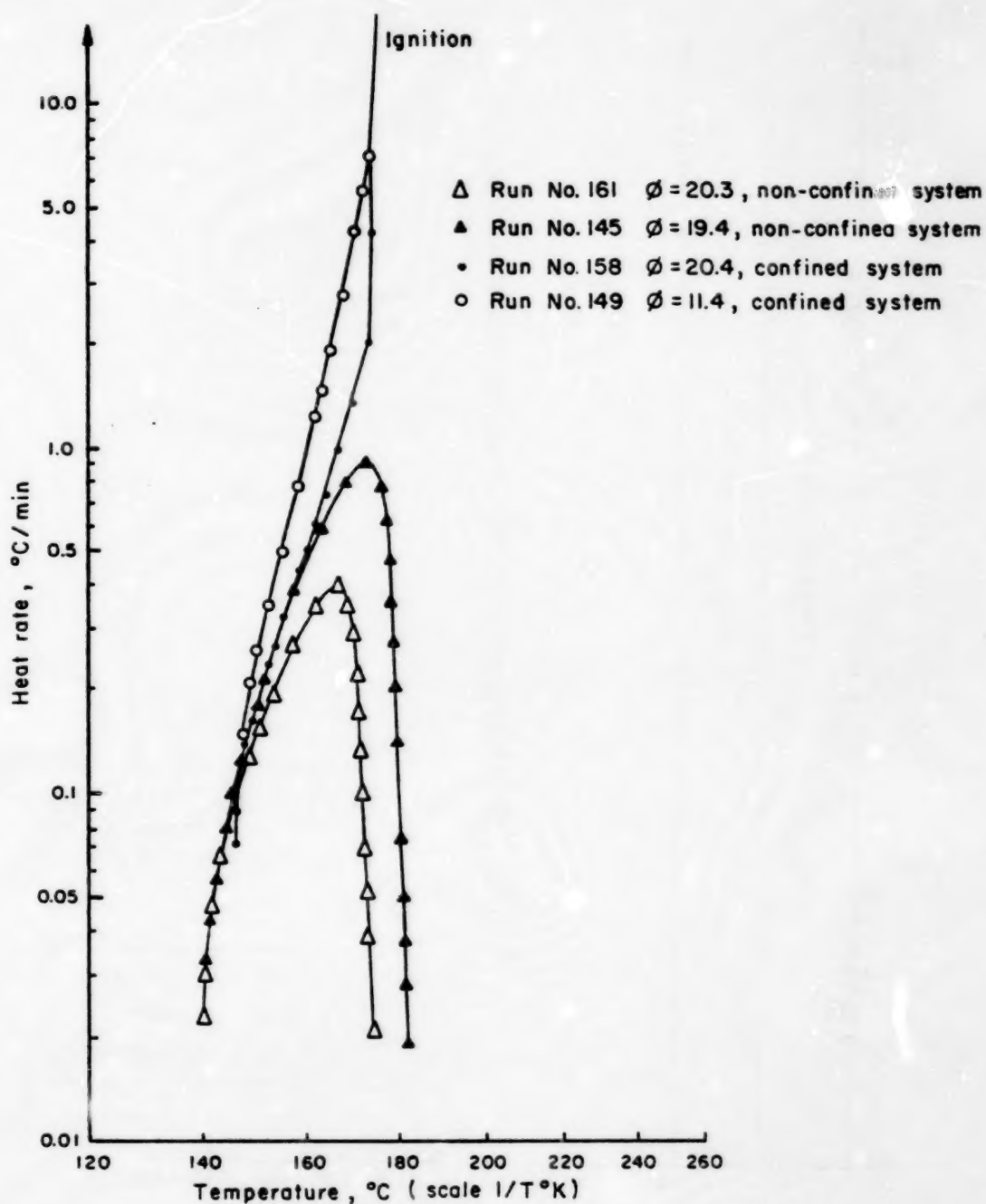


Fig. 6 - PETN, comparison among ARC experiments of ϕ effect and experimental system, light weight Hastelloy C spherical bomb, air atmosphere, $50^{\circ}C$ start temperature, $5^{\circ}C$ stop heat interval, 30 minutes wait time.

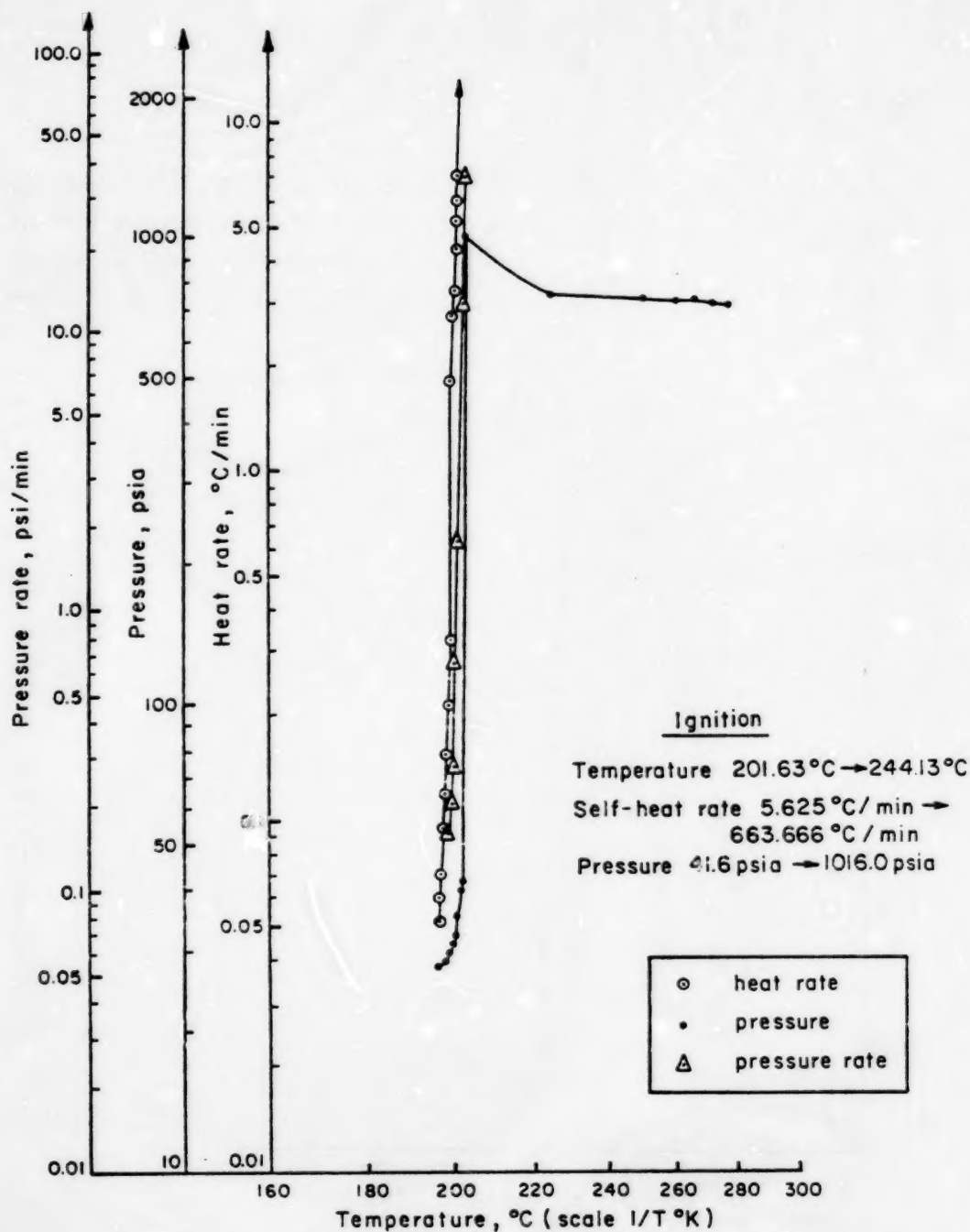


Fig. 7 - RDX, data plots from ARC experiment run no. 154, confined system, sample 0.2640g, $\phi=18.0$, 18.5700g Hastelloy C spherical bomb, air atmosphere, 190°C start temperature, 2°C step heat interval, 30 minutes wait time.

where A represents RDX, B represents $\text{H}_2\text{C} = \text{N} - \text{NO}_2$, C represents $(\text{CH}_2\text{O} + \text{N}_2\text{O})$ or $(\text{HCN} + \text{HNO}_2)$ and D represents the final products.

The exotherm of Tetryl decomposition was detected at 141°C with reproducibility. Apparently, decomposition takes place in two major stages with a short and slow exothermic peak in between as shown in Fig. 8. After the self-heat rate of the first exothermic peak increased to a maximum rate, it slowed down before the second major exotherm occurred. This agrees with the results of other investigators that Tetryl decomposes with two exothermic peaks by DSC [8]. However, the initial decomposition temperature detected is lower than the literature data. Activation energy for the first peak was calculated by using the equation derived for the singular reactions from the reaction order plot. The values for Run no. 150, 152, 155 and 156 are 59.3 kcal/mole, 60.8 kcal/mole, 59.9 kcal/mole and 54.3 kcal/mole respectively. These values are in reasonable agreement with those obtained using DSC. The calculated activation energy indicated Tetryl initially decomposed according to a singular reaction then followed by complex reactions. By increasing the sample weight, thermal inertia ϕ was reduced. Figure 9 is the plot of a Tetryl decomposition in which explosion occurred when ϕ was reduced to 7.4. This resulted in a rupture of the sample bomb and a certain degree of damage to the calorimeter. Figure 10 demonstrates that a larger ϕ will lower the observed final temperature and self-heat rates. By the non-confined system, without pressure effect, the initial decomposition was also detected at 141°C but the maximum self-heat rate was lower.

TNT was heated initially to 50°C , then searched for exothermic decomposition after equilibrium at 5°C intervals. The decomposition was detected at 226°C with ϕ equal to 20. Figure 11 shows the plots of TNT decomposition data such as heat rate, pressure and pressure rate versus temperature using a confined system. Pressure increased drastically at 254°C accompanied by a fast ignition. The ϕ effect and the experimental system are compared among the ARC runs for TNT decomposition in Fig. 12. It indicated that the test with lower ϕ had lower initial temperature with fast ignition at decomposition. Comparing the result to the other investigators, the initial decomposition temperature detected by ARC was lower. TNT tested by non-confined system had a maximum self-heat rate of only $1.5^\circ\text{C}/\text{min}$ even though the initial temperature was also detected at 226°C . After decomposition, the weight loss was about 70% with black residue remaining in the sample bomb.

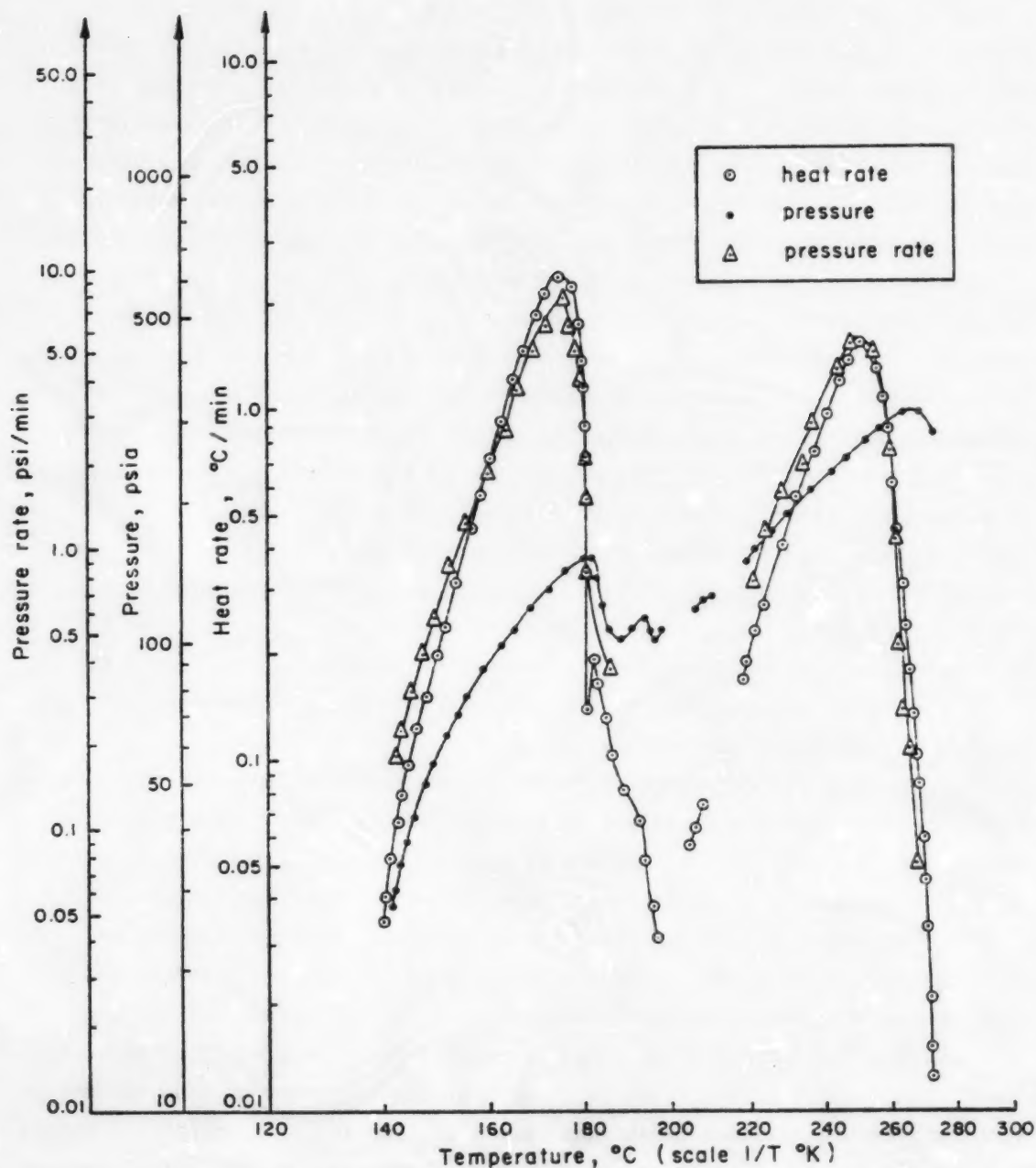


Fig. 8 - Tetryl, data plots from ARC experiment run no. 156, confined system, sample 0.4265 g, $\phi = 11.8$, 19.0115 g Hastelloy C spherical bomb, air atmosphere, 50°C start temperature, 5°C heat step interval, 30 minutes wait time.

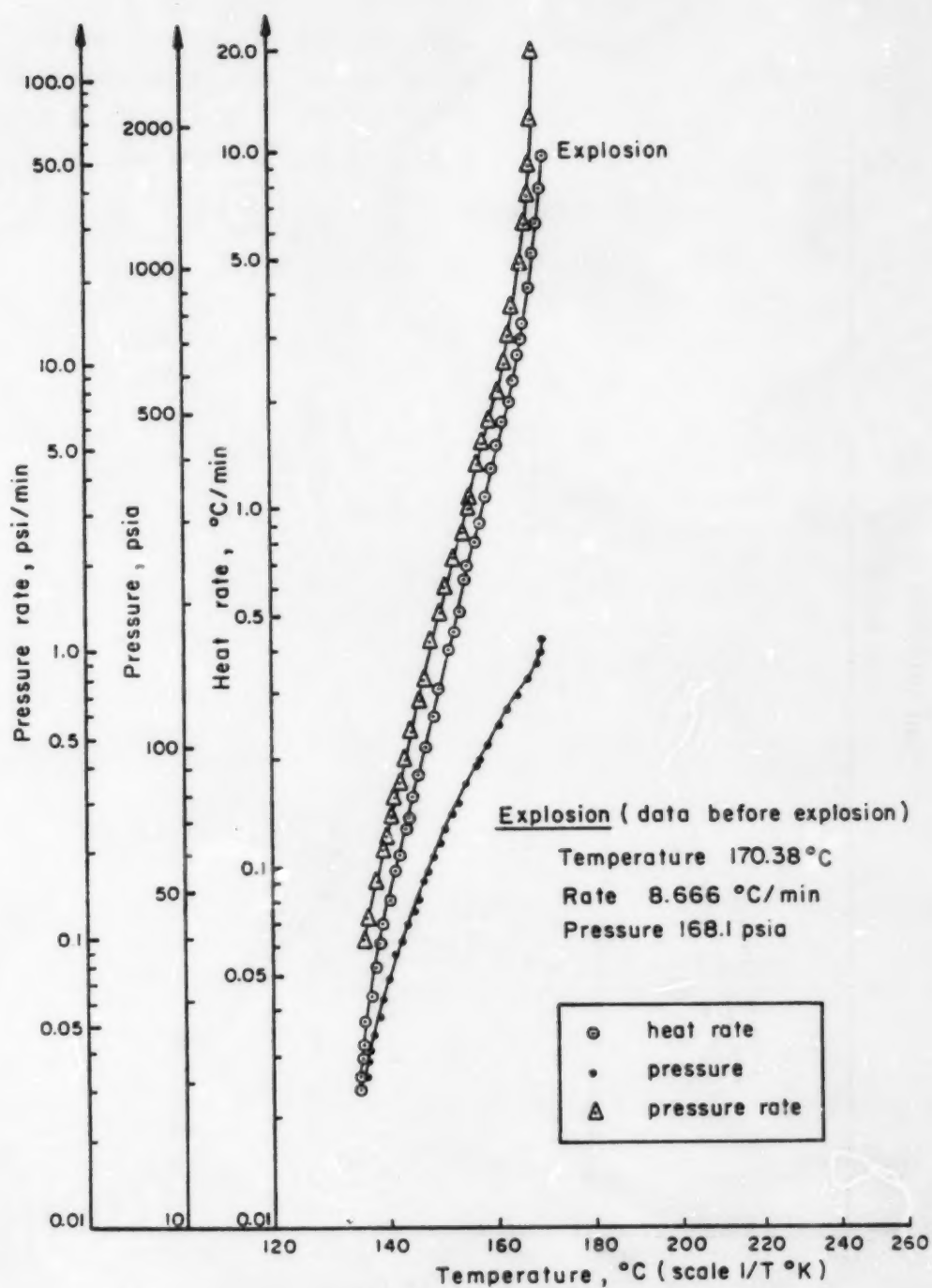


Fig. 9 - Tetryl, data plots from ARC experiment run no. 155, confined system, sample 0.7300 g, $\phi = 7.4$, 19.3412 Hastelloy C spherical bomb, air atmosphere, 50°C start temperature, 5°C heat step interval, 30 minutes wait time.

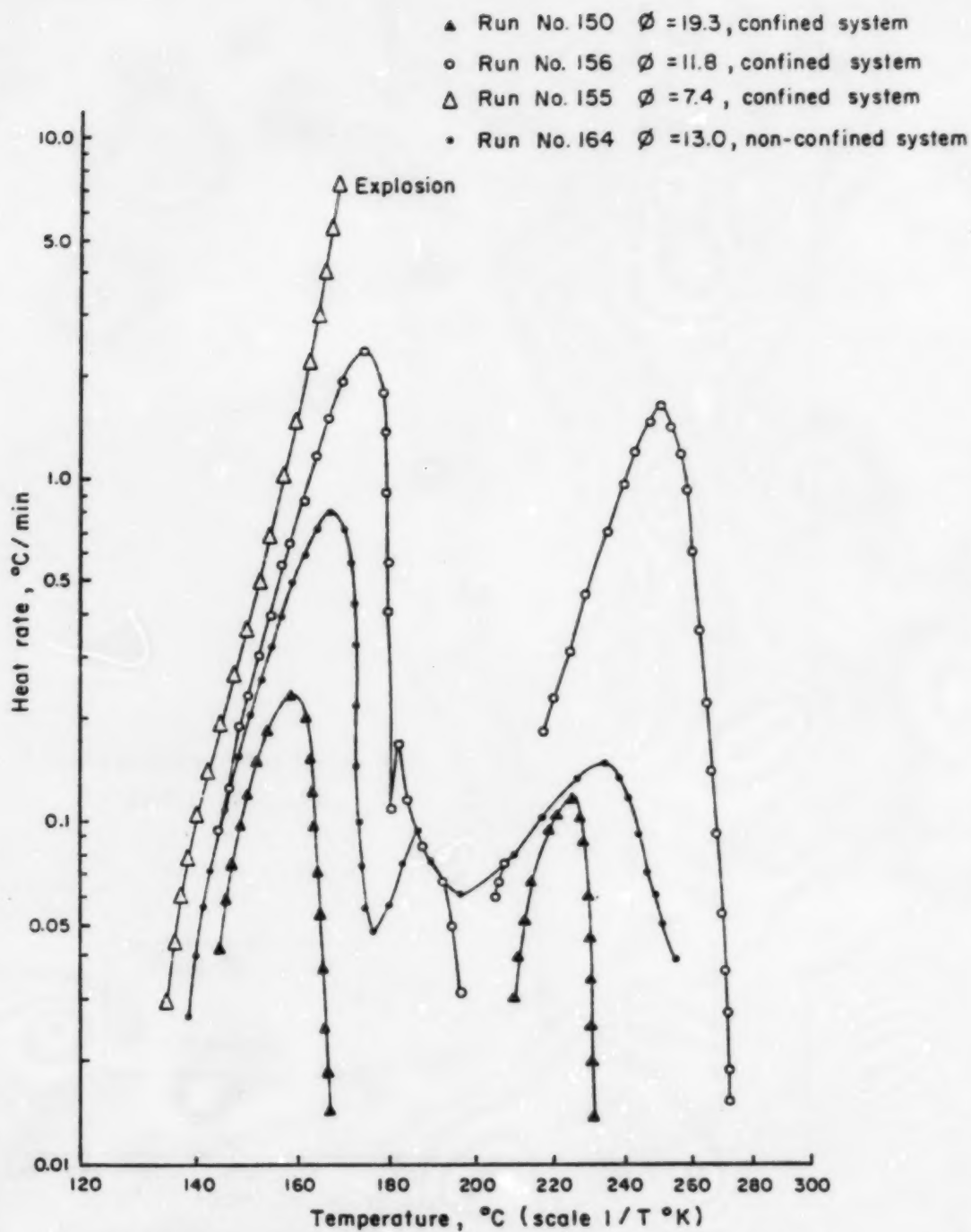


Fig. 10 - Tetryl, comparison among AkC experiments of ϕ effect and experimental system, light weight Hastelloy C spherical bomb, air atmosphere, 50°C start temperature, 5°C step heat interval, 30 minutes wait time.

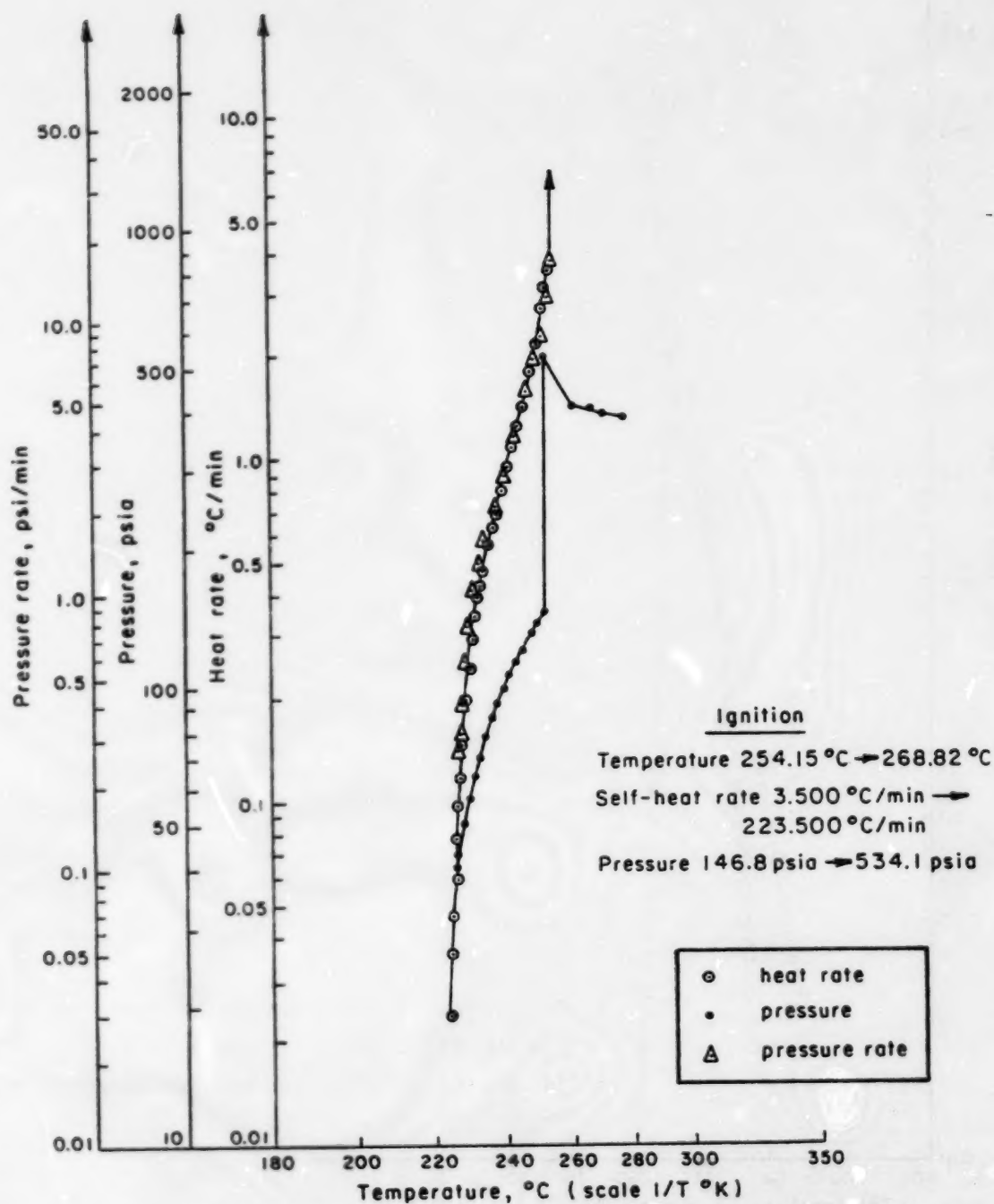


Fig. 11 - TNT, data plots from ARC experiment run no. 159, confined system, sample 0.2337 g, $\phi = 20.4$, 18.7380 g Hastelloy C spherical bomb, air atmosphere, 50°C start temperature, 5°C step heat interval, 30 minutes wait time.

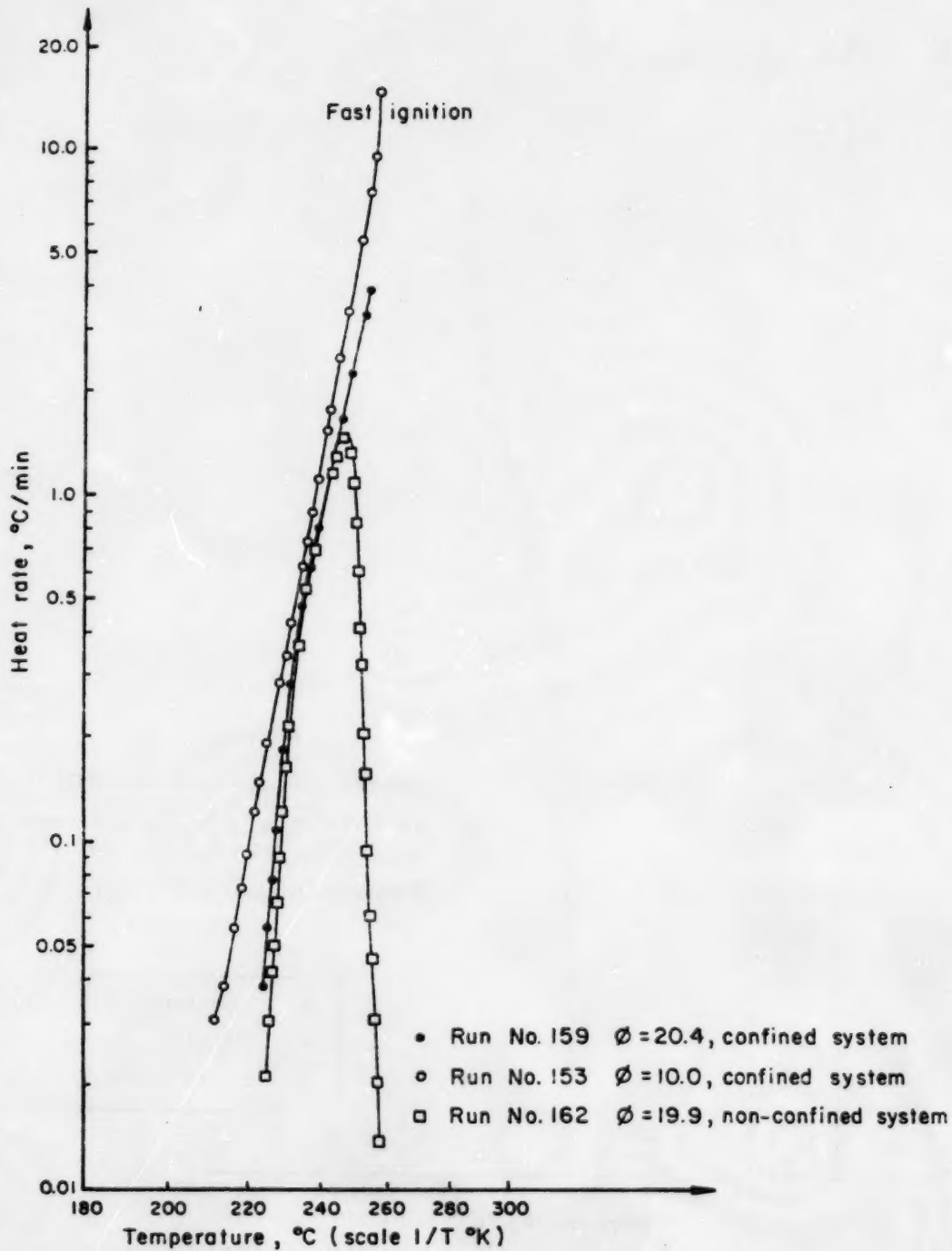
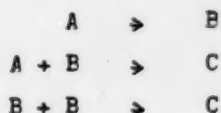


Fig. 12 - TNT, comparison among ARC experiments of $\varnothing$ effect and experimental system, light weight hastelloy C spherical bomb, air atmosphere, 50°C start temperature, 5°C step heat interval, 30 minutes wait time.

As reviewed by Guidry [23], the kinetic studies of TNT decomposition indicate that the process is an autocatalytic one in which a reactive intermediate is formed which subsequently reacts with TNT molecules to produce gaseous reaction products. Therefore TNT is modeled as an autocatalytic three reaction process,



where A represents TNT, B represents the reactive intermediate and C represents the final products. The fact that the decomposition results obtained for TNT using a non-confined system had no ignition may be due to the loss of reactive intermediate products or demonstrate a pressure effect.

Thermal decomposition data for Nitroguanidine were rarely found in the literature. One result was reported that the decomposition occurred at 200°C-204°C using a DSC technique [9].

Step heat experiments were performed on Nitroguanidine by ARC for the decomposition studies with both confined and non-confined systems. Figure 13 shows the results obtained using a confined system. The sample decomposed at 166°C with a self-heat rate of 0.058°C/min. When the self-heat rate increased, the pressure also increased and the ignition occurred at 171°C. However, the adiabatic temperature rise of the system was 15°C and the weight loss after ignition was only 65%. As shown in Fig. 14, the experimental system had a great effect on the decomposition. The duplicate runs by confined system indicated the decomposition was detected at about 166°C then followed by an ignition. The test by non-confined system had a slow exotherm detected at about 200°C which was remarkably higher than the initial temperature by confined system.

Guanidine nitrate was also tested for its thermal stability by ARC with a confined system. Some difficulties arose due to blockage of the pressure measurement line by the molten sample. Therefore no accurate pressure data could be obtained and no detailed studies were pursued using this system. Two tests by step heat method were done and consistent initial decomposition temperatures were detected at 251°C which is above the melting point.

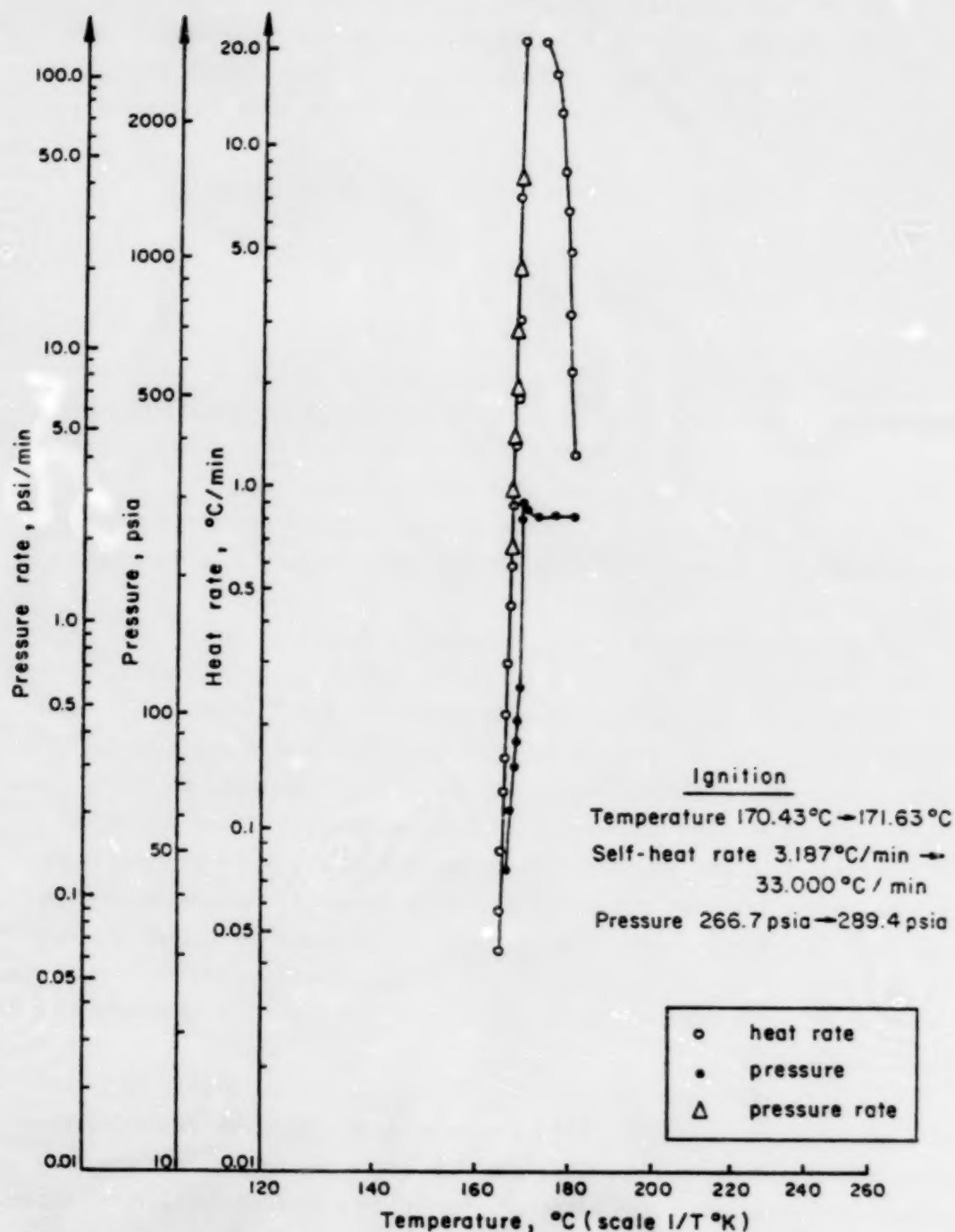


Fig. 13 - Nitroguanidine, data plots from ARC experiments run no. 171, confined system, sample 0.2538 g, $\phi = 17.8$, 17.3700 g Hastelloy C spherical bomb, air atmosphere, 50°C start temperature 5°C step heat interval, 30 minutes wait time.

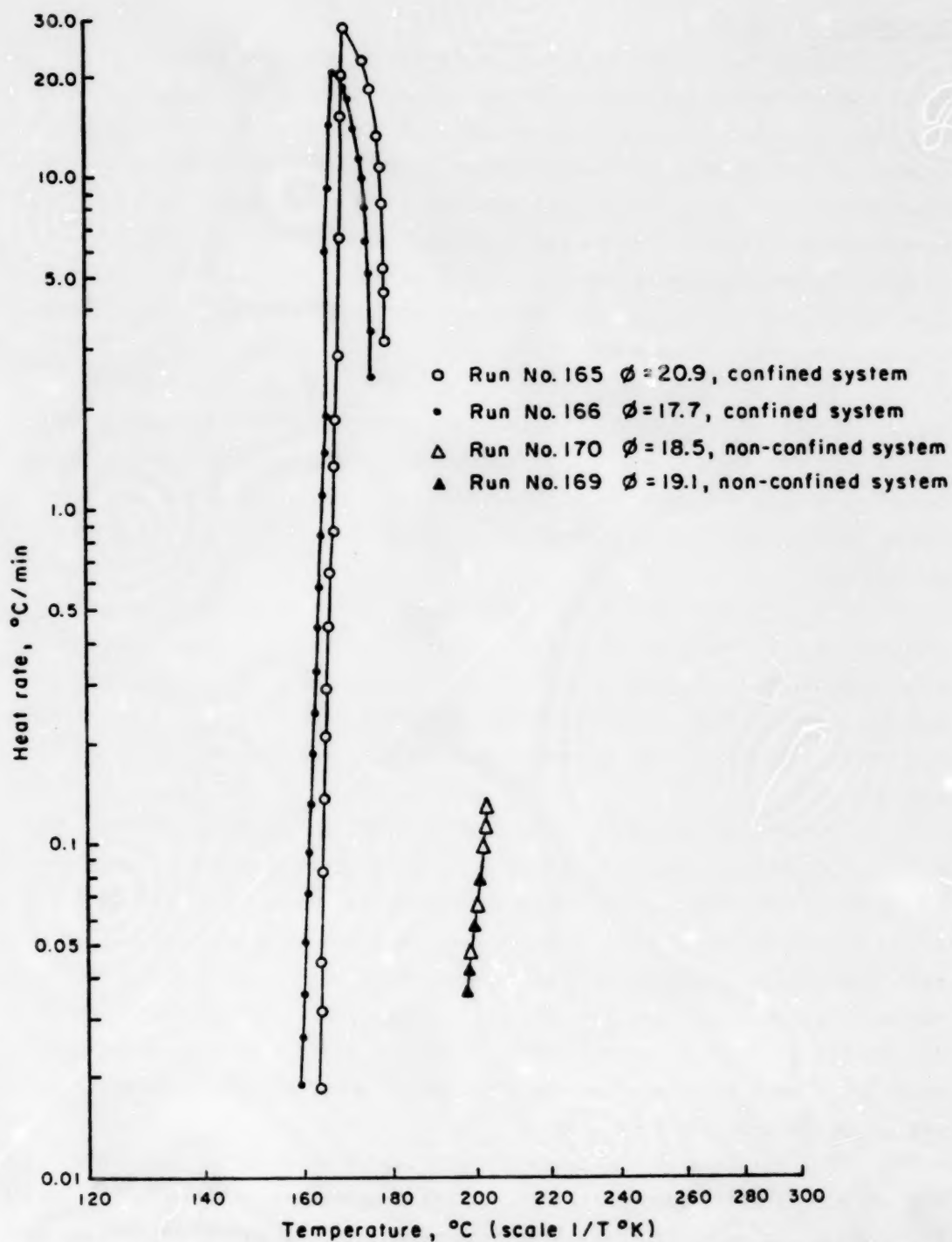


Fig. 14 - Nitroguanidine, comparison among ARC experiments of ϕ effect and experimental system, light weight Hastelloy C spherical bomb, air atmosphere, 50°C start temperature, 5°C step heat interval, 30 minutes wait time.

ISOTHERMAL AGE STUDIES

Isothermal aging tests were performed on six high explosives for 600 min. The isothermal age temperature was chosen to be 5°C below the initial temperature detected by step heat method. If the sample survived the isothermal period, it was step heated 5°C to generate the self-heat curve. A Hastelloy C light weight spherical bomb was loaded with sample and hooked up tightly to the pressure transducer which was termed "confined" system. The temperature-temperature rate-pressure data were collected automatically whenever the self-heat rate was greater than 0.02°C/min. Table 4 lists the isothermal decomposition data by ARC.

PETN was isothermally aged at 135°C and 130°C. It survived for 200 min at 135°C then the exotherm occurred at 137°C. However, the sample was stable at 130°C for 600 min. Both tests showed PETN ignited with very fast temperature rate and pressure build-up to over 400 psia at ignition. The decomposition curve patterns were similar in both step heat and isothermal age methods.

As indicated by the step heat logic, PDX was unstable at 195°C. However, it was stable at 190°C for 600 min. The self-heat curve occurred after step heat 2°C intervals (at 199°C with heat rate 0.365°C/min) and ignited vigorously with pressure build-up to 500 psia. Figure 15 compares the ARC data generated by isothermal age and step heat methods which appear similar.

Tetryl was heated to 135°C, 130°C, 125°C and left isothermally for 600 min. Exothermic reaction was detected as soon as the temperature reached 135°C and 130°C. The decomposition took place in two major stages and fast ignition occurred at the second major decomposition with pressure build-up to over 1000 psia. Figure 16 is the temperature vs time plot which demonstrates two major temperature increases during the decomposition. Tetryl was stable for 600 min at 125°C isothermal aging. Decomposition was detected at 136°C after 5°C step heat intervals. No ignition occurred and pressure build-up was below 200 psia for both stages.

The exotherm of TNT decomposition was detected after 380 min at 215°C and 420 min at 210°C isothermal aging. The temperature before ignition was at 241°C which was lower than the step heat method. TNT ignited vigorously with pressure build-up to about 750 psia. Decomposition curve patterns were similar for both heating methods.

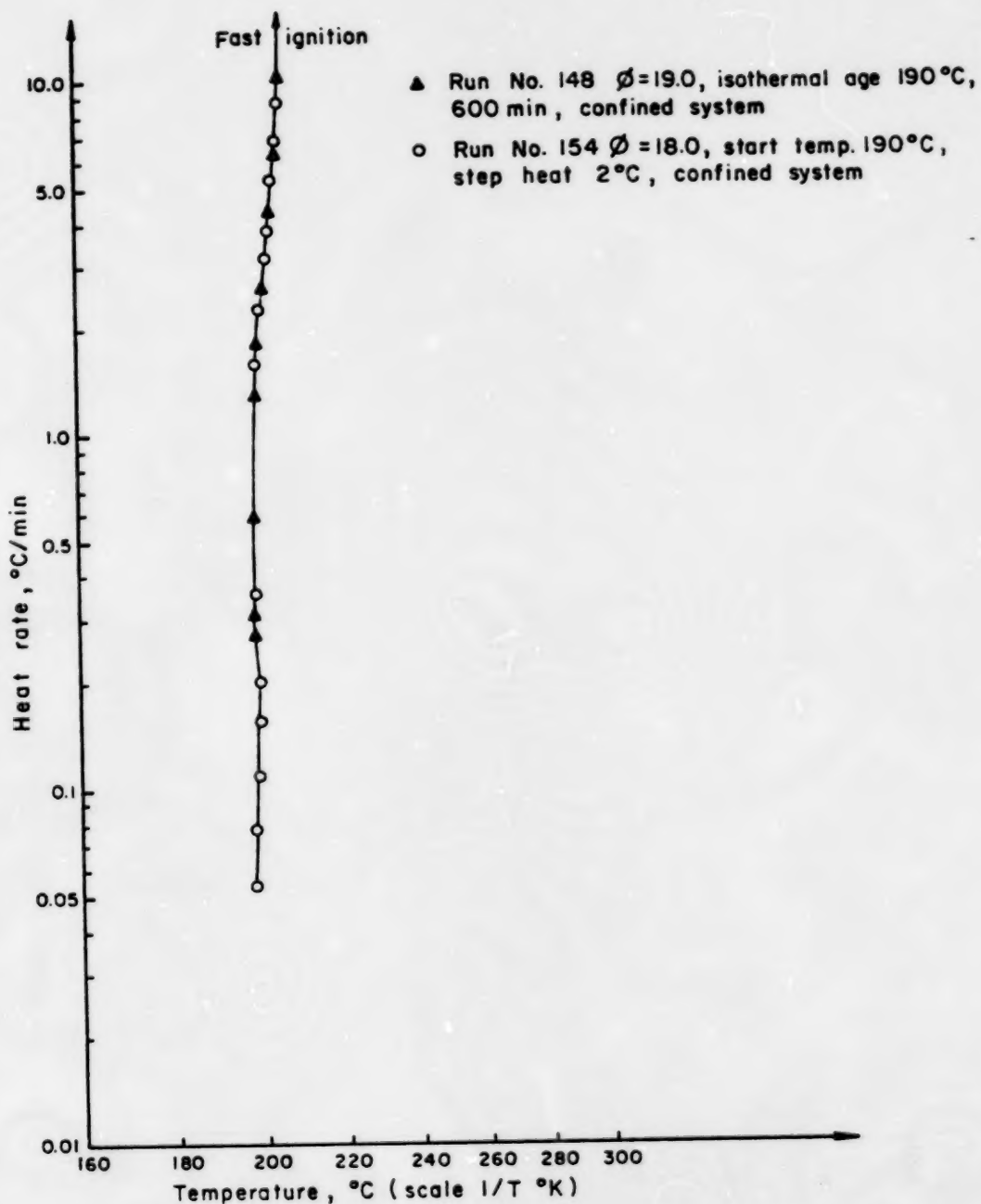


Fig. 15 - RDX, comparison among ARC experiments under different heat methods, light weight Hastelloy C spherical bomb, air atmosphere.

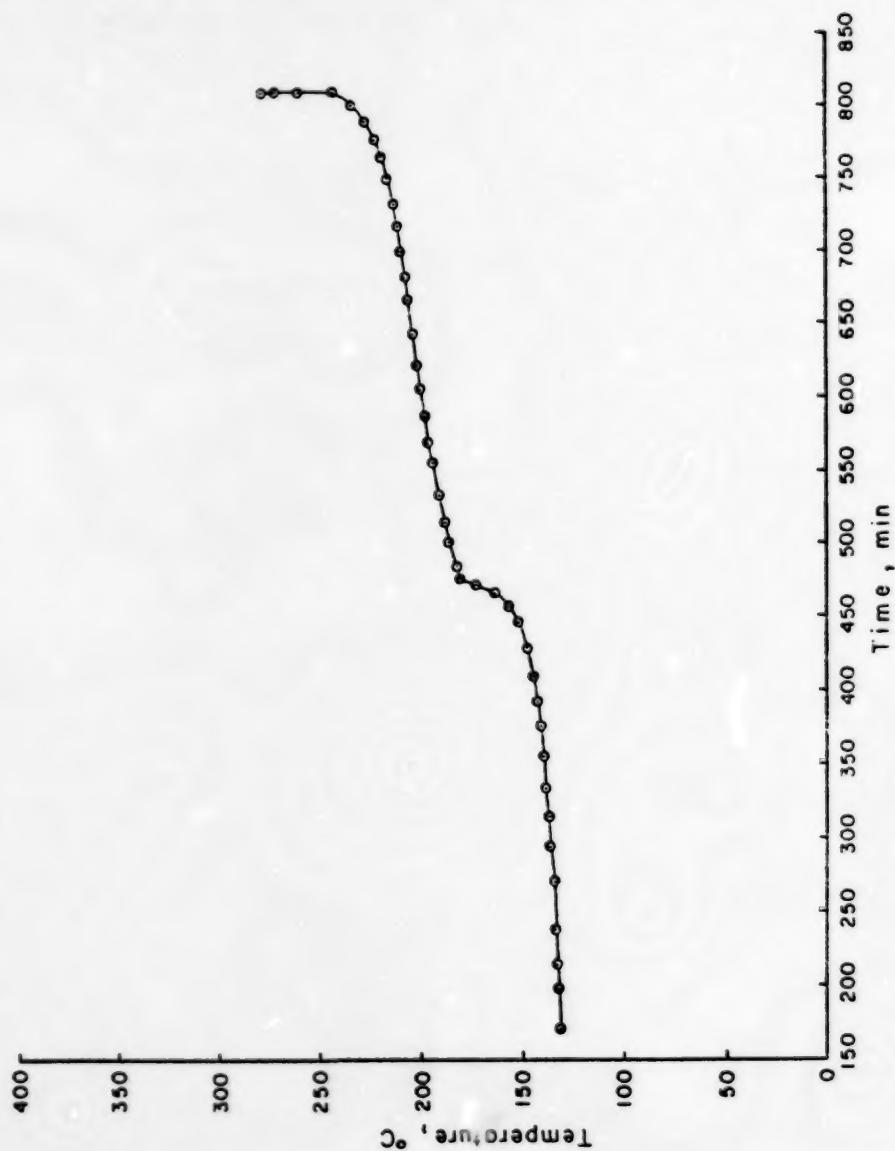


Fig. 16 - Tetryl, temperature vs time plot from ARC experiment run no. 179, $\phi = 10.4$, 19.0115 g Hastelloy C spherical bomb, air atmosphere, isothermal age at 130°C for 600 min., 5°C step heat interval, 30 minutes wait time.

Table 4 - Thermal stability study of high explosives by isothermal age for 600 minutes

Run no.	a	Run parameters		Initial data			Before ignition			At maximum rate				ΔT _{AB,S} (°C)	Wt loss %	
		Iso age (°C)	Stable time (min)	T _o (°C)	m _o (°C/min)	t _o (min)	T (°C)	m (°C/min)	P (psia)	P (MPa)	T _m (°C)	m _m (°C/min)	P _m (psia)			P _m (MPa)
PETN																
172	19.1	135°C	200 min	137.40	0.036	290.16	166.93	8.500	67.5	0.47	197.69	473.500	435.8	3.00	78.74	-
181	19.7	130°C	600 min	141.66	0.051	697.32	169.25	7.833	159.1	1.10	192.79	369.000	507.9	3.50	72.00	97.9
RDX																
148	19.0	190°C	600 min	198.96	0.365	720.53	205.61	9.333	29.6	0.20	231.69	326.000	504.4	3.48	62.13	-
TETRYL																
167	11.3	135°C	0 min	137.57	0.029	80.47	no ignition				176.12	3.333	169.1	1.17	-	-
				continuous curve			250.61	4.600	503.3	3.47	262.44	182.333	1343.5	9.26	143.46	81.0
179	10.4	130°C	0 min	133.03	0.019	170.61	no ignition				175.10	2.222	142.8	0.98	-	-
				continuous curve			243.04	1.826	194.7	1.34	259.94	261.000	1005.6	6.93	146.04	92.5
183	9.9	125°C	600 min	136.51	0.037	699.43	no ignition				175.56	3.214	125.1	0.86	-	-
				continuous curve			no ignition				256.02	3.333	182.4	1.26	163.34	76.7
TNT																
168	19.0	215°C	380 min	220.03	0.091	426.14	241.08	3.666	146.8	1.01	260.10	242.857	775.0	5.34	52.54	78.7
182	19.1	210°C	420 min	217.05	0.022	456.57	241.09	3.000	124.3	0.86	258.18	273.333	746.7	5.15	56.16	81.4
Nitroguanidine																
178	18.0	155°C	200 min	157.76	0.024	244.35	163.26	3.285	168.3	1.16	164.36	27.000	231.5	1.60	15.48	66.1
180	18.0	150°C	600 min	166.20	0.042	740.82	171.93	3.190	172.9	1.19	173.71	14.000	180.0	1.24	12.45	63.4
Guanidine nitrate																
177	11.3	240°C	0 min	242.41	0.047	43.46	no ignition				317.03	2.625	blockage	-	82.63	99.7

Isothermal aging tests were performed at 155°C and 150°C for 600 min on Nitroguanidine. The sample only survived 200 min at 155°C but it was stable for 600 min at 150°C. Consistent initial decomposition temperature was detected at 166°C similar to step heat method and the pressure build-up was about 200 psia. After ignition, weight loss was in the 60% to 70% range.

Only one isothermal decomposition study was performed at 240°C for 600 min on Guanidine nitrate. No stable isothermal aging was obtained and the exotherm started at 242°C with maximum self-heat rate 2.6°C/min. No accurate pressure could be monitored due to blockage of the pressure line by the molten sample.

ANALYSIS OF ORIGINAL SAMPLES AND RESIDUES

The infrared spectra of six high explosives, the black residue of TNT and Tetryl and the white residue of Nitroguanidine were prepared as KBr pellets. They were compared with the original explosives in Fig. 17, 18 and 19. Most of the absorption bands disappeared in the infrared spectra of the residues. As the weight loss of PETN, RDX and Guanidine nitrate was over 90% after the thermal decomposition, not much residue could be recovered. Only the infrared spectra of original compounds were prepared and shown in Fig. 20. Some characteristics have been found very useful for the infrared identification of explosive ingredients [24]. The organic nitrates show two strong sharp bands at 6.0 and 7.8 microns and a broad band at about 12.0 microns. Phenyl groups have two bands at 6.23 and 6.70 microns. Aromatic nitro compound shows two strong bands at about 6.4 and 7.4 microns.

The residues of TNT, Tetryl and Nitroguanidine were analyzed by C, H, N elemental analyzer. These are compared with theoretical values for the original compounds in Table 5. Unfortunately, it is difficult to deduce any chemical structures of the residues based on these two analytical techniques. Further investigations will be carried out in the near future.

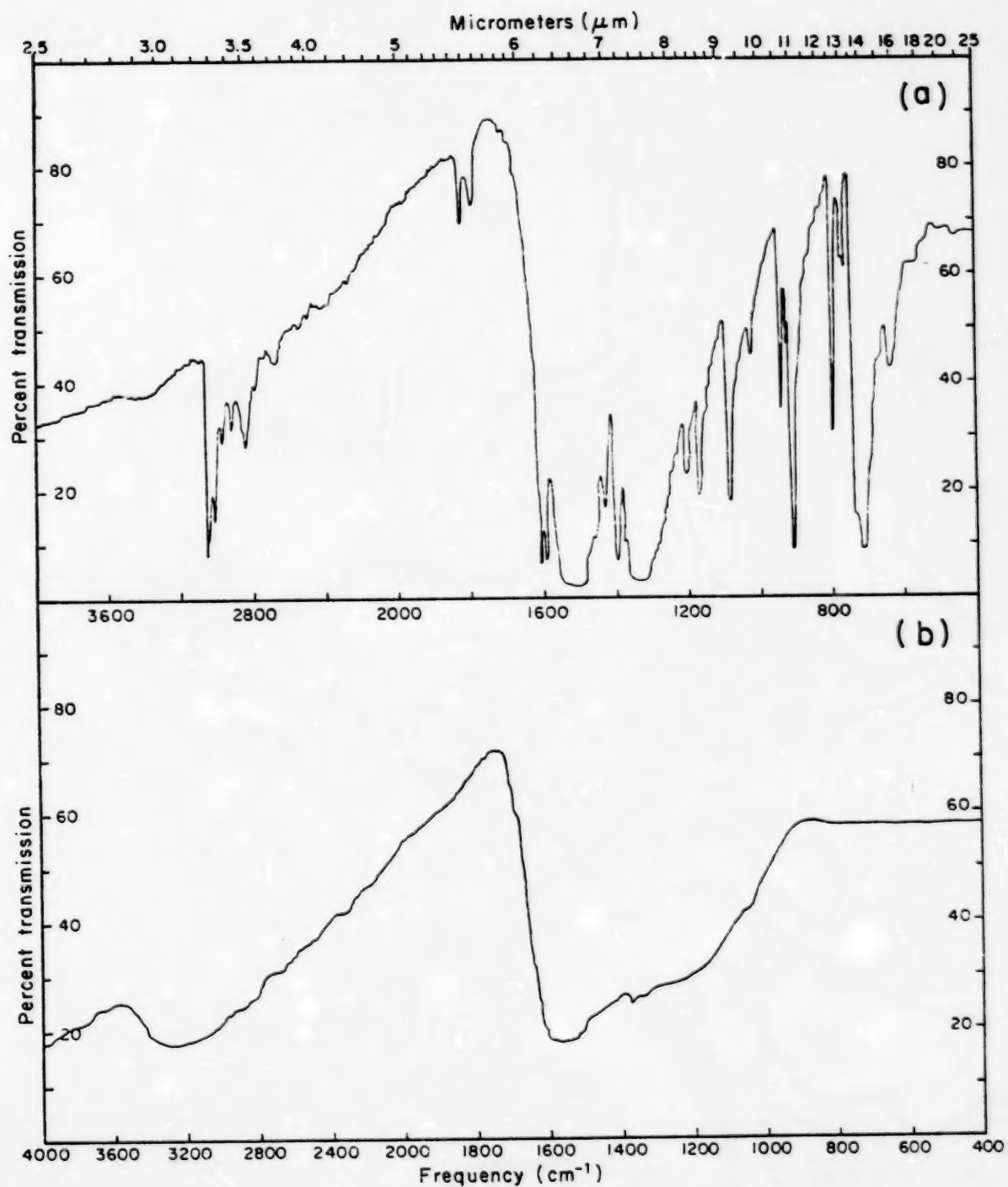


Fig. 17 - Infrared spectra of (a) TNT, (b) thermal decomposition residue, in KBr pellet.

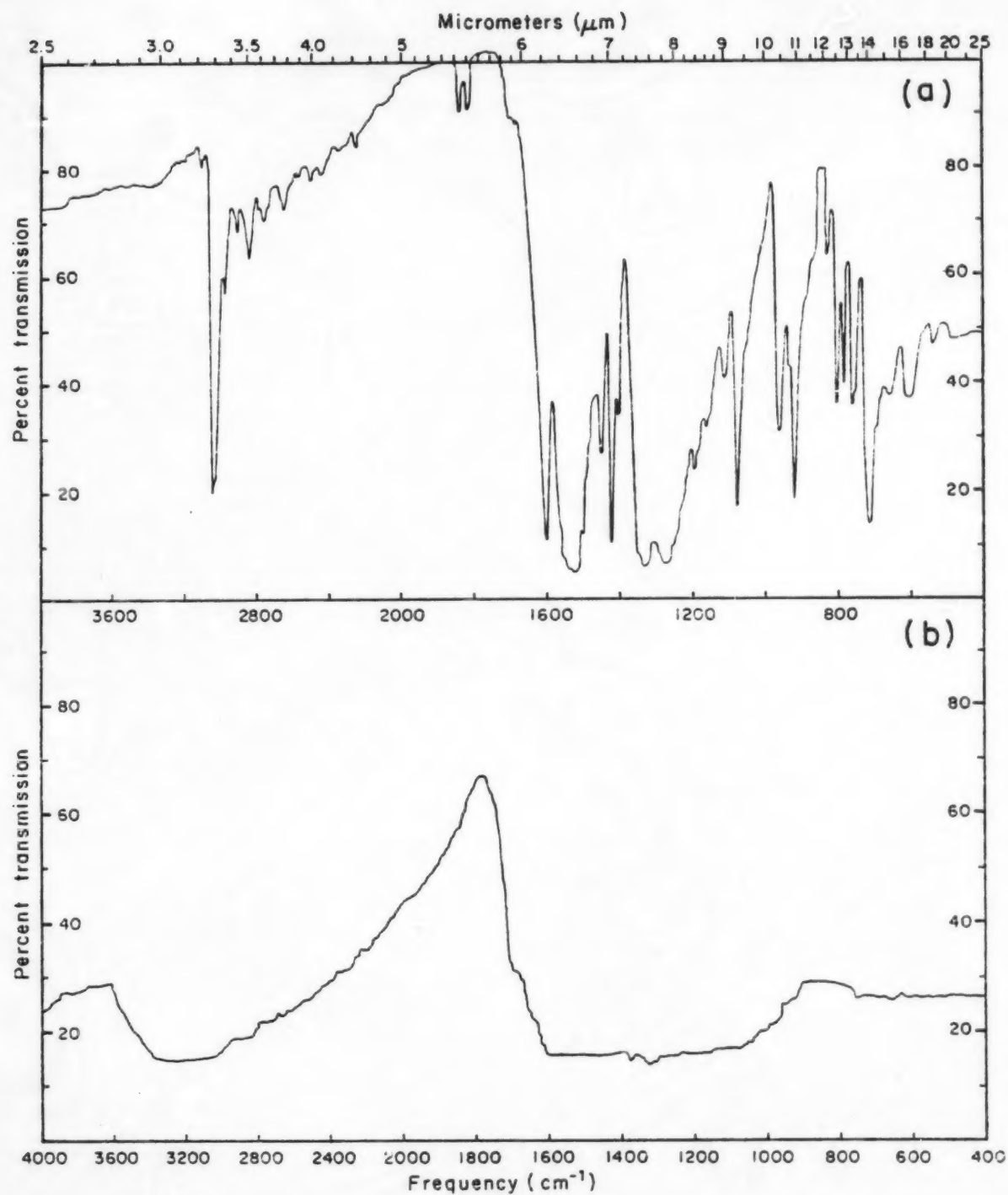


Fig. 18 - Infrared spectra of (a) tetryl, (b) thermal decomposition residue, in KBr pellet.

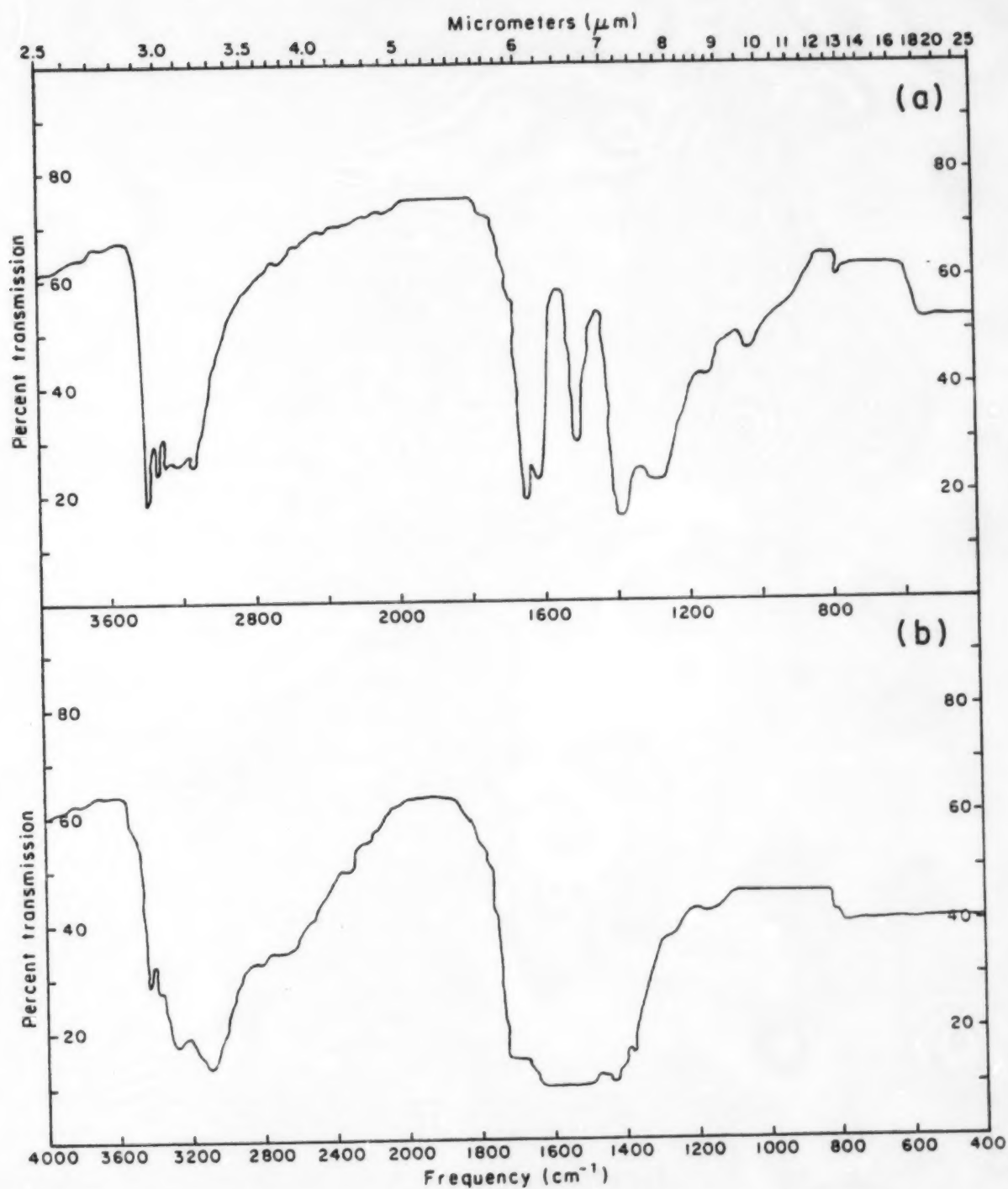


Fig. 19 - Infrared spectra of (a) nitroguanidine (b) thermal decomposition residue after ignition, in KBr pellet.

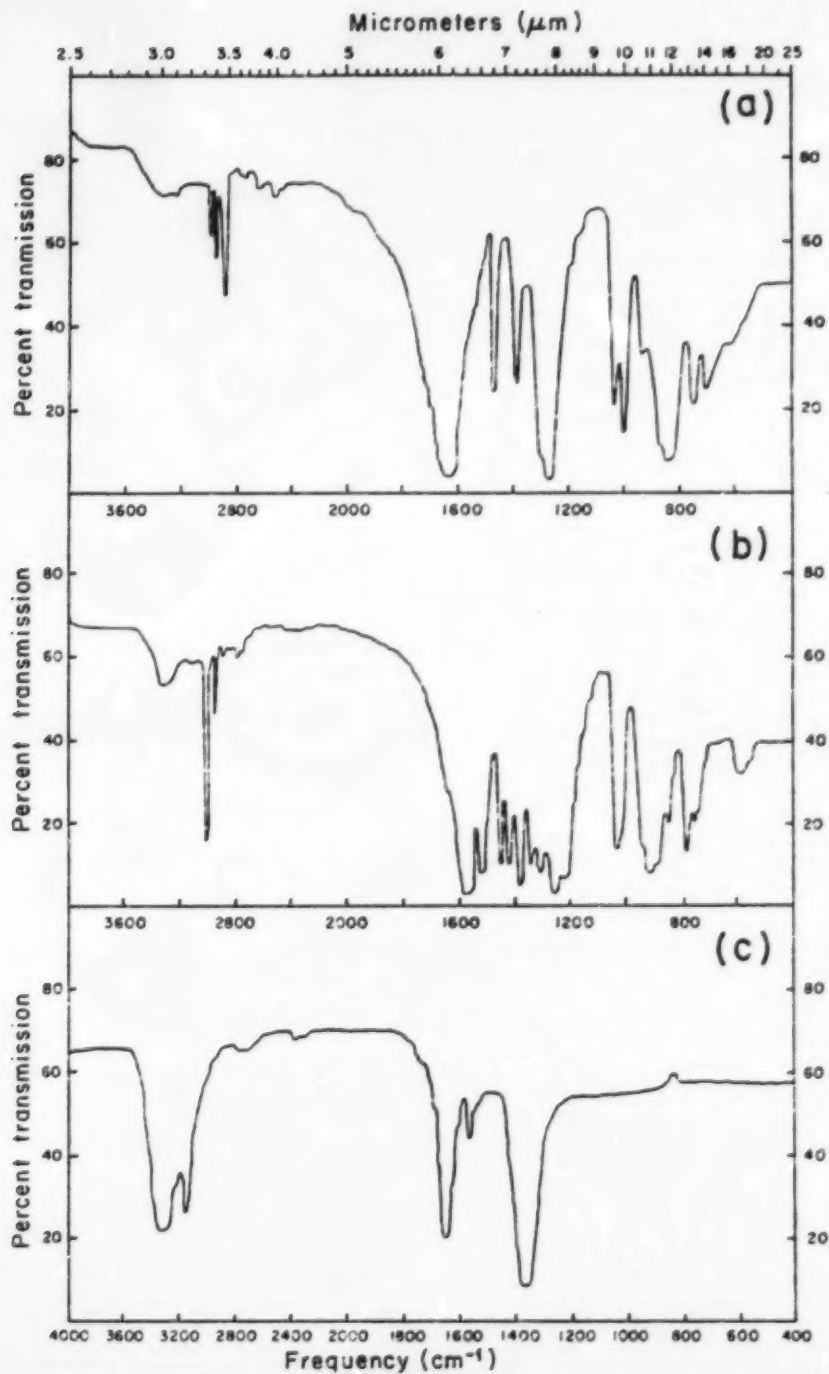


Fig. 20 - Infrared spectra of (a) PETN, (b) RDX, (c) guanidine nitrate, in KBr pellet.

Table 5 - Analytical results of explosives and residues by C, H, N elemental analyzer

ARC run no.	Sample	mol. wt	C%	H%	N%
-	TNT	227.13	37.02	2.22	18.50
159	TNT residue	-	59.39	2.49	18.17
-	Tetryl	287.15	29.28	1.76	24.39
152	Tetryl residue	-	56.46	2.17	17.80
-	Nitroguanidine	104.07	11.54	3.87	53.84
165	Nitroguanidine residue, fast decomposition	-	29.45	3.67	58.15
169	Nitroguanidine residue, slow decomposition	-	30.75	3.24	59.78

CONCLUSIONS

As demonstrated in this paper, the accelerating rate calorimetric technique is unique in providing information concerning temperature and pressure of reactions taking place under adiabatic conditions. TNT, Tetryl and Guanidine nitrate melt before the thermal decomposition takes place. PETN melts with decomposition but RDX and Nitroguanidine decompose in the solid state. Also the pressure effect on decomposition can be demonstrated by the decomposition pattern using two systems. Generally the maximum decomposition rate is slower using the non-confined system. The onset decomposition temperatures are summarized in Table 6. Comparing the results by ARC to the other literature data, the decomposition temperature is detected earlier by using ARC.

The ARC is designed primarily for the analysis of homogeneous liquids. In order to achieve reliable results, the sample must exhibit high thermal conductivity. The solid state decomposition can vary tremendously with changes in crystal perfection and purity. It may yield non-conservative results as to the runaway reaction hazards. Since evaluation of rate data at high self-heat rates is complex due to the measurement lag in the normal detection system, only data in the low self-heat rate region should be used. The deviations are observed at about 20°C/min for light weight Hastelloy C spherical bomb [2].

Table 6 - Summary of the decomposition data for high explosives using ARC and step heat logic

Sample	ϕ	Melting point (°C) literature values	Exp. confined system		Exp. non-confined system	
			Initial temp (°C)	Ignition	Initial temp (°C)	Ignition
PETN	~20	141.3	147	yes	141	no
RDX	~19	204	>195	yes	>195	yes
Tetryl	~12	128.4	141	no	141	no
TNT	~20	80.6	226	yes	226	no
Nitroguanidine	~19	232	166	yes	199	no
Guanidine nitrate	~18	215	252	no	-	-

The kinetic data is not extracted from the tests because the decompositions are not simple. It is recognized that many chemical reactions encountered in the hazard study cannot be kinetically modeled because of their natural complexity. However, thermodynamic quantities, such as the heat of reaction and final pressure can be evaluated, since they depend only upon the initial and final states of the chemical system.

ACKNOWLEDGEMENTS

The authors wish to thank D. Dinel for preparing the infrared spectra.

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NOTATION

E	activation energy
C_v	average heat capacity
M	mass
ϕ	thermal inertia
T	temperature
T_o	initial temperature
T_m	temperature at maximum self-heat rate
$\Delta T_{AB,S}$	adiabatic temperature rise for the total system
m	self-heat rate
m_o	initial self-heat rate
m_m	maximum self-heat rate
t	time
t_o	initial time
P	pressure
P_m	pressure at maximum self-heat rate